

A KINETIC STUDY OF THE TRANSFORMATION GRAPHITE \rightleftharpoons LINEAR CARBON FORMS BY X-RAY DIFFRACTION*

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This paper is a progress report on one of the aspects of the continuing research at Aerospace on the carbon phase diagram and the linear carbon forms. Our work and the results of other investigators suggest that the carbon phase diagram has the general form shown in Figure 1. This figure is intended to be more illustrative than quantitative since certain features have been exaggerated to make them easier to discuss. The dashed line designated JANAF represents the vapor pressure of graphite would have if it were the stable form up to the melting point. Because the linear forms are the stable forms, their vapor pressure lies below the JANAF curve everywhere. Since the difference between the vapor pressure of the linear forms and the JANAF curve is small, it is one of the features that has been exaggerated.

The research reported here concerns the transformations graphite \rightleftharpoons linear form No. 1 and linear form No. 1 \rightleftharpoons linear form No. 2 along the solid-vapor boundary. The graphite \rightleftharpoons linear form No. 1 transformation occurs near 2600 K, linear form No. 1 \rightleftharpoons linear form No. 2 occurs near 2500 K, and the third transformation occurs at 3050 K. It has been known for several years that a number of observations suggested that the transformation rates for rising temperature are much lower than the rates of the reverse transformations. Recently, it was found that these transformations could be followed by x-ray diffraction; this made it possible to acquire quantitative data on the rate constants.

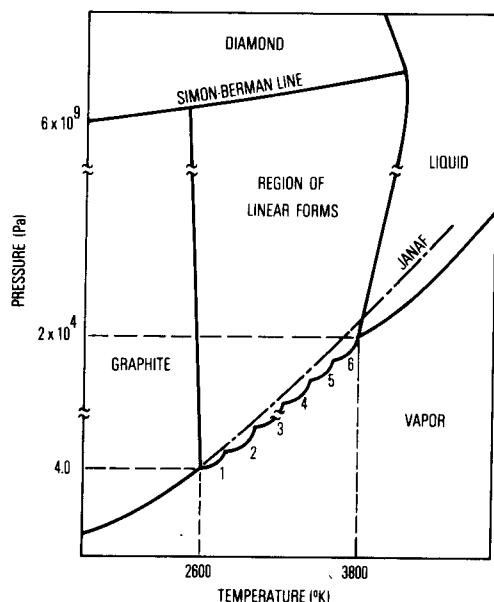


Figure 1. Carbon Phase Diagram

The apparatus used for this work was a General Electric XRD-5 diffractometer equipped with a fixture for heating pyrolytic graphite (PG) samples resistively in an argon atmosphere so that the x-ray reflection could be measured while the sample was hot. The PG was oriented such that the x-ray reflection was from the basal plane edges. Intensity of the reflection from the (010) planes was followed as a function of time for several hours. At the end of this period, the diffractometer was set to the graphite (002) reflection and then the heating current was turned off. No (002) reflection was detectable at the end of the heating period. However, several minutes after turning off the heating current, the (002) reflection started to increase as the linear forms transformed back to graphite. As a first approximation, it was assumed that the rate of intensity decrease of the (010) reflection was proportional to the rate of transformation of graphite to linear form and that the transformation was a first-order reaction. Rate constants calculated on this basis are given in Table 1. The linear form to graphite transformation gave a typical first-order decay curve and it was analyzed by the established methods for such cases. Although the accuracy of these data in Table 1 are probably good only to order of magnitude, they quantitatively confirm the previous qualitative observations on relative transformation rates.

Identification of the linear forms is not complete but is expected to be ready for the July presentation. Also, as more experiments are carried out, the transition temperatures will be more accurately located.

Table 1. Rate Constants for Carbon Transformations

Transformation	Temperature (°K)	Rate Constant (1/sec)
Graphite/linear form No. 1	2680	2.2×10^{-5}
Graphite/linear form No. 2	2840	5.1×10^{-5}
Linear form No. 2/graphite	~300	2.6×10^{-2}
Linear form No. 1/graphite	~300	1.9×10^{-3}

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